LOW-LEAD-CONTENT PLATING PROCESS

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the priority benefit of Taiwan application serial no. 90128069, filed November 13, 2001.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a low-lead-content plating process. More specifically, the present invention relates to a low-lead-content plating process, in which the crystal phase re-organization of the final plated layer can be improved and the melting point of the final plated layer can be decreased by infrared-ray reflow process.

15 Description of the related art

To reduce the discharge of toxic contaminants in the environment, many efforts are made to reduce lead substance in manufacture production. Many approaches have been put into practice, such as "lead free" gasoline. In the developed countries, since

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1982, related rules have been made to prevent the solder (Sn85Pb15) pollution. Solder material is common in the semiconductor, electronic and photoelectric industries. For example, Japanese electronic appliance regulation restrains the use of lead before the year of 2001, and the EC legislative (WEEE) announces the similar. However, in consideration of the effective implementation of these regulations, these countries extend the executable period by 4 to 8 years, because effective "lead free" plating technology needs to be developed.

Currently, tin lead alloy (Sn₈₅Pb₁₅) is widely used as an electric connection in IC packaging, PCBs, diodes and active/passive devices.

For the future "lead free" requirement, an infrared-ray reflow tin/lead plating and the like have been proposed, such as Sn/Cu plating, Sn/Bi plating or Sn/Ag plating. However, these plating processes have not been put into practice yet.

In the conventional Sn/Cu bath, Sb/Bi bath and Sn/Ag bath, copper, bismuth and silver are deposited on an anode, a titanium basket and a PP board. The deposition of these metals is resulted from the standard oxidation potential of the copper, bismuth and silver E^0_{Cu} , E^0_{Bi} , E^0_{Ag} that are higher than that of tin E^0_{Sn} .

The reactions of tin, copper, bismuth and silver are shown in the following formula (1), (2), (3) and (4). The redox reactions in the tin/copper bath, tin/bismuth bath and

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tin/silver bath are shown in the following formula (5), (6) and (7).

$$Sn \rightarrow Sn^{2+} + 2e^{-}$$
 $E^{0}_{Sn} = -0.14V$ (1)

$$Cu \rightarrow Cu^{2+} + 2e^{-}$$
 $E^{0}_{Cu} = 0.34V$ (2)

$$Bi \rightarrow Bi^{3+} + 3e^{-}$$
 $E_{Bi}^{0} = 0.2V$ (3)

$$Ag \rightarrow Ag^{+} + e^{-} \qquad E^{0}_{Ag} = 0.8V \qquad (4)$$

$$Cu + Sn^{2+} \rightarrow Cu^{2+} + Sn$$
 $E_{Cu}^{0} - E_{Sn}^{0} = 0.38V$ (5)

$$2Bi + 3Sn^{2+} \rightarrow 2Bi^{3+} + 3Sn$$
 $E_{Bi}^{0} - E_{Sn}^{0}^{2+} = 0.34V$ (6)

$$2Ag + Sn^{2+} \rightarrow 2Ag^{+} + Sn$$
 $E_{Ag}^{0} - E_{Sn}^{0}^{2+} = 0.94V$ (7)

In formula (5), (6) and (7), copper ions, bismuth ions and silver ions are naturally reduced and deposited on the anode and the PP board in the conventional bath due to the plus difference of $(E^0_{Cu} - E^0_{Sn}^{2+})$, $(E^0_{Bi} - E^0_{Sn}^{2+})$ and $(E^0_{Ag} - E^0_{Sn}^{2+})$. Therefore, the final plated product has a composition of substantially pure tin.

In general, the anode and the PP board are non-conductive. Dual charged tin ions are the ions that are adsorbed onto the surface of the non-conductor. Therefore, the anode and the PP board that are dipped in a solution containing the dual charged tin ions would be charged. If the potential of the induced charged ions is higher than that of the existent dual charged tin ions, then the ions are more quickly and substantially adsorbed onto the anode and the PP board.

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However, in order to avoid the use of lead, a pure tin plating process has been proposed to coat on pin members of assembly. The melting point of tin may arise during infrared-ray reflow, such that the heat resistance of the whole assembly has to be improved. Unfortunately, it is not practical in the current related industries.

5 Furthermore, the pure tin plating process still has several disadvantages, such as short service life, long whiskers, poor phase rearrangement, and poor solderability.

SUMMARY OF THE INVENTION

In one aspect of the present invention, a low-lead-content plating process is provided, in which lead, thallium and iron ions in the order of ppm are added into a pure tin plating liquid to change the molecule orientation during infrared-ray reflow, thereby reducing the melting point of the plating liquid.

Further, the present invention also provides a low-melting-point low-lead-content plating process, in which a final plated layer with excellent polymerization and thus improved solderability can be obtained by re-organizing the crystal phase using the infrared-ray reflow process.

In the present invention, the concentration of tin ions in the plating liquid is in the range of 25 to 75 mg/l, lead ions is in the range of 2.5 to 10,000 mg/l, thallium ions in

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the range of 1 to 550 mg/l, and iron ions in the range of 1 to 550 mg/l. When the concentration of the lead ions is in the appropriate range, the final plated layer has a lead content which complies with the international "lead free" standard, i.e. 600-2000 ppm (about 30 to 120 mg/l). Furthermore, under control of the concentration of lead ions, a final plated layer with tin/lead of 99/l can be obtained.

In the plating liquid of the present invention, a brightener, methane sulfonic acid and deioned water can be further added. The concentration of the brightener is in the range of 50 to 250 mg/l. The concentration of methane sulfonic acid is in the range of 80 to 250 mg/l.

The final plated layer formed by the low-lead-content plating process of the present invention has a melting point decreased to about 212°C and has no whisker.

The final plated layer with tin/lead of 99/1 obtained by the present invention has a melting point lowered to about 205°C.

The plating process of the present invention is compatible with any current plating process, such as barrel plating, rack plating, PCB plating, strip-to-strip plating and reel-to-reel plating. Therefore, the plating process of the present invention can be combined with those processes recited above and performed by any suitable type of the plating apparatus, such as barrel plater, rack plater, PCB plater, strip-to-strip plater, and

reel-to-reel plater.

It is to be understood that both the foregoing general description and the following detailed description are exemplary, and are intended to provide further explanation of the invention as claimed.

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BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings are included to provide a further understanding of the invention, and are incorporated in and constitute a part of this specification. The drawings illustrate embodiments of the invention and, together with the description, serve to explain the principle of the invention. In the drawings,

Fig. 1 shows a comparison between the physical properties of the pure tin bath, tin/silver bath, tin/copper bath, tin/bismuth bath and tin/lead bath obtained by the prior art and that obtained by the present invention;

Fig. 2 shows a comparison between the conventional plated layer and the final plated layer according to the present invention; and

Fig. 3 shows a low-melting-point pure tin plating process and apparatus therefor.

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DESCIPTION OF THE PREFERRED EMBODIMENT

Reference will now be made in detail to the present preferred embodiments of the invention, examples of which are illustrated in the accompanying drawings. Whenever possible, the same reference numbers are used in the drawings and the description to refer to the same or like parts.

In one preferred embodiment of the present invention, tens to hundreds ppms of lead, thalliun and iron ions are added into a pure tin electroplating liquid. The concentration of tin ion is in the range of 2.5 to 10,000 mg/l. The concentration of lead ions is in the range of 1 to 550 mg/l. The concentration of iron ions is the range of 1 to 550 mg/l. When the concentration of lead ions is in the range of 5 to 120 mg/l, the final plated layer has a lead content much less than the amount required by the international "lead free" standard, 600 to 2000 ppm (about 30 to 120 mg/l). When the concentration of lead ions is about 2500 mg/l, a final plated layer with 99/l of tin/lead ratio can be obtained.

In this embodiment of the present invention, the composition of the final plated layer is listed as follows:

Majority	Majority
	Wiajority
25-100,000	25-50,000
10-5,500	10-2,500
10-5,500	10-2,500
	10-5,500

Additional to the above lead, thallium and iron ions, a brightener, methane sulfonic acid and deioned water can be added into the plating bath. The concentration of the brightener is in the range of 50 to 250 mg/l. The concentration of the methane sulfonic acid is in the range of 80 to 250 mg/l. Any commercially available brightener can be used in the present invention.

In this embodiment of the present invention, the reactions of tin, lead, thallium, and iron are shown in formula (8), (9), (10) and (11). The redox reactions in tin/copper, tin/bismuth, and tin/silver bathes are shown in formula (12), (13), and (14).

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$$\rightarrow$$
 Sn²⁺ + 2e⁻ $E_{Sn}^0 = -0.14V$ (8)

$$Pb \rightarrow Pb^{2+} + 2e^{-}$$
 $E_{Pb}^{0} = -0.2V$ (9)

$$Fe \rightarrow Fe^{3+} + 3e^{-}$$
 $E^{0}_{Fe} = -0.18V$ (10)

$$Tl \rightarrow Tl^{2+} + 2e^{-}$$
 $E^{0}_{Tl} = -0.2V$ (11)

$$Pb + Sn^{2+} \rightarrow Pb^{2+} + Sn$$
 $E_{Pb}^{0} - E_{Sn}^{0}^{2+} = -0.06V$ (12)

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$$2Fe + 3Sn^{2+} \rightarrow 2Fe^{3+} + 3Sn$$
 $E_{Fe}^{0} - E_{Sn}^{0}^{2+} = -0.04V$ (13)

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$$T1 + Sn^{2+} \rightarrow T1^{2+} + Sn$$
 $E_{Sn}^{0}^{2+} = -0.06V$ (14)

In the formula (12), (13) and (14), due to the minus electric potential difference $(E_{Pb}^0 - E_{Sn}^{0-2+})$, $(E_{Fe}^0 - E_{Sn}^{0-2+})$ and $(E_{Tl}^0 - E_{Sn}^{0-2+})$, lead, iron and thallium ions in the plating liquid are deposited on the anode and the PP board in the plating bath, rather than be reduced.

Fig. 1 shows comparison between the physical properties of the pure tin bath, tin/silver bath, tin/copper bath, tin/bismuth bath and tin/lead bath obtained by the prior art and that obtained by the present invention. The final plated layer obtained from the low-lead-content bath has a solderability comparable with that obtained from conventional tin/lead bath but superior to that obtained from pure tin bath, tin/silver bath, tin/copper bath and tin/bismuth bath. Furthermore, the final plated layer obtained from the low-lead-content plating has a lower melting point, no whisker and excellent stability.

Because the lead, thallium and iron ions added in the pure tin plating liquid can change the orientation of molecular bond during infrared-ray reflow, the melting point of the plating liquid can be lowered. Lead, thallium and iron ions in the pure tin plating liquid allow a crystal phase reform of the final plated layer to obtain denser

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orientation. Therefore, the solderability of the final plated layer can be increased.

Moreover, lead, thallium, iron ions in the plating liquid can have various concentrations to either adjust the density of the final plated layer during the crystal phase reorganization or change the melting point of the final plated layer during infrared-sray reflow.

Fig. 2 shows a comparison between the conventional plated layer and the final plated layer of the present invention. In the prior art, tin/lead alloys with tin/lead ratio of 85/15, 99/1 and 100/0 have melting points of 212°C, 228°C and 232°C, respectively. However, in the present invention, tin/lead alloys with tin/lead ratio of 85/15, 99/1 and 100/0 have the melting points of 183°C, 205°C and 212°C, respectively. The final plated layer obtained by the present invention, even with alloy ratio similar to those of the prior art, still has lowered melting points due to lead, thallium and iron ions added in the pure tin plating liquid. The final plated layer having a lowered melting point provides advantages to the manufacture process. For example, a thermal process is not required in the infrared-ray reflow process to increase the temperature up to 232°C, which is one serious concern with respect to heat resistance of the device.

Fig. 3 shows a low-melting-point pure tin plating process and apparatus therefor.

The plating process of the present invention is compatible with any current plating

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process, such as barrel plating, rack plating, PCB plating, strip-to-strip plating and reel-to-reel plating. Therefore, the plating process of the present invention can be combined with above-mentioned processes and performed by means of any suitable type of the plating apparatus, such as barrel platers, rack platers, PCB platers, strip-to-strip platers, and reel-to-reel platers.

. The process of the present invention can be applied to related industries, such as bumping on a wafer, manufacture of PCB, packaging of an integrated circuit, packaging of a transistor/diode, manufacture of an active/passive device and photoelectric device.

In view of the foregoing, the "lead free" plating process of the present invention provides at least the following advantages over the prior art. The molecule bond is rearranged when the reflow process is performed by using infrared ray, thereby the melting point of the final plated layer being lowered. The crystal phase reorganization of the final plated layer allows not only to lower the melting point of the final plated layer, but also generate no whisker. In addition, the final plated layer has lowered lead content, which is submitted to the international "lead free" standard and complied with the environment protection.

It will be apparent to those skilled in the art that various modifications and variations can be made to the structure of the present invention without departing from

the scope or spirit of the invention. In view of the forgoing, it is intended that the present invention cover modifications and variations of this invention provided they fall within the scope of the following claims and their equivalents.